STUDIES ON THE USE OF COULOMETRIC AND AMPEROMETRIC ANALYSIS

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ABSTRACT

A coulometric titration is described in which unipositive thallium is oxidized to the tripositive state by electrolytically generated bromine or chlorine. The end-point is determined amperometrically by measuring the current between two platinum electrodes with an impressed potential difference of 200 millivolts. Confirmatory analyses have shown an accuracy of 0.2% for 93 to 200 microgram samples, and of 0.1% for samples of from 200 to 1900 micrograms.

The application of dual intermediates to secondary coulometric titrations with an amperometric end point has been studied. Cupric copper and bromide have been used for the alternate electrolytic generation of bromine and cuprous copper for the purpose of titrating a substance exhibiting a slow rate of reaction with bromine. A procedure is described by which aniline has been titrated in quantities of from 13 to 280 micrograms with an average error without regard to sign of less than 0.4 micrograms.

A study has been made of the bromine-bromide diffusion current, the effects of the concentrations of bromine, bromide and hydrogen ion; the minimum bromide ion concentration necessary to maintain generation of bromine with 100% current efficiency was determined.

Studies have been made of the diffusion-controlled currents observed when potential differences, less than the decomposition potential, are impressed upon two platinized-platinum electrodes in solutions of hydrochloric acid which are 0.1 VF in potassium chloride and saturated with hydrogen gas. The effects of the electrode size and material, the applied potential, and the presence of oxygen and nitrogen gas are described.

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PART I

COULOMETRIC TITRATION OF THALLIUM WITH EITHER BROMINE OR CHLORINE AND AN AMPEROMETRIC END POINT

COULOMETRIC TITRATION OF THALLIUM WITH EITHER BROMINE OR CHLORINE AND AN AMPEROMETRIC END POINT

Coulometric titrations by means of electrolytically generated bromine have been described by Ernest H. Swift and co-workers[2,5,6,11]. This method involves passing a known constant current for a measured time between two platinum electrodes immersed in a solution containing a soluble bromide and the substance to be determined. The reducing substances studied, thiodiglycol, tripositive arsenic, tripositive antimony and iodide are oxidized by the bromine and the end point is determined by observing the current flow between a second pair of platinum electrodes (the indicator electrodes), which have a small potential difference impressed across them.

Neither thiodiglycol nor tripositive arsenic or antimony and their oxidized forms set up reversible half cells at the generator or the indicator electrodes under the conditions of the titration. No indicator current flows between the indicator electrodes until the titration end point has been reached and bromine is generated in excess. However, the iodide-iodine and thallous-thallic half-cells are reversible at the platinum electrodes. An indicator current flows throughout the titration reaching a maximum near to the time when iodide and iodine or Tl(I) and Tl(III) are in equal concentrations. By shielding the generator cathode, it was possible to apply the secondary coulometric method to substances involving reversible half-cell reactions. A method

for the determination of small quantities of thallium has been developed.

Reagents

Sodium bromide solutions, 1.0 VF (volume formal), were prepared from the reagent grade salt.

Sixty percent reagent grade perchloric acid was used.

Eight formal hydrochloric acid solutions were prepared from the reagent grade concentrated acid.

Freshly boiled distilled water was used in all solutions.

Electrolytic oxidation of blank solutions described below indicated reducing impurities in the hydrochloric acid solution. The effect was removed by boiling the acid with the calculated amount of 3% hydrogen peroxide.

Five grams of pure thallium metal were dissolved in hot concentrated nitric acid and evaporated nearly to dryness. Ten milliliters of concentrated perchloric acid were added and the solution evaporated ; a second portion of the concentrated perchloric acid was added and the fuming was repeated. The thallic perchlorate which precipitated on cooling was dissolved in boiled water containing perchloric acid to give a solution approximately 0.1 VF in thallic perchlorate and 1 VF in perchloric acid. A stock solution of thallous perchlorate was prepared from a portion of the thallic perchlorate by reduction with sulfur dioxide followed by boiling to remove the excess sulfur dioxide. The thallous perchlorate was standardized against a standard solution of potassium

iodate using an iodine monochloride end point according to the method of Swift and Garner[10].

Apparatus

The apparatus used was that described by Meier, Myers and Swift[5] with the substitution of a simple voltage-regulated rectifier connected to the alternating current line through a voltage-regulating Sola transformer in place of the direct current supply. The generator cathode was contained within a glass shield open at the top and terminating at the bottom in a "fine" porosity sintered glass disc and filled above the level of the surrounding solution with 2 VF perchloric acid. Shielding the cathode from the body of the solution eliminated the danger of reduction of the thallium salts, and indicator currents caused by the presence of hydrogen gas in the titrated solution were avoided.

The linear dimensions of the indicator electrodes were approximately 1.5 by 1.5 cm. and 2.7 by 2.3 cm., the larger being the cathode. A potential difference of 200 millivolts was impressed across the indicator electrodes when titrating with bromine and 300 millivolts when titrating with chlorine. Experiments have indicated that these values lay in the range in which the diffusion current was nearly independent of fluctuations in the applied potential.

Titrations were made in 40 x 80 mm. weighing bottles and at a solution volume of 40 milliliters.

The titration instrument provided three rates of generation although only two were used in this work. The high rate corresponded to about 10 x 10^{-8} equivalents per second and the low rate about 1 x 10^{-8} equivalents per second. The generator circuit was calibrated by measuring with a student potentiometer the potential drop across a standard 199.8 ohm coil from a resistance box. The standard cell was occasionally checked against a Weston cell calibrated by the U.S. Bureau of Standards.

Procedure

The oxidizing or reducing impurities in the reagents were determined by titrating blank solutions. For each bromide blank, five milliliters of 1 VF sodium bromide, five milliliters of 60% (9VF) perchloric acid and thirty milliliters of water were placed in a titration cell. In the case of chloride blanks, five milliliters of 8 VF hydrochloric acid and thirty five milliliters of water were added. The indicator potential was set at 200 or 300 millivolts and the generator current passing through the dummy resistance was adjusted to the desired value. Bromine or chlorine was generated for short intervals of time depending upon the rate of generation used (0.5 seconds for the high rate, 5 seconds for the low rate). Ten seconds were allowed after each interval of generation before the current and the generation time were recorded. The linear portion of the plot of indicator current vs. time of generation (from 10 to 40 microamperes) was extrapolated to zero current. The value

of the generator time intercept was designated as the blank time. Several blanks were run and the average value used for the impurity correction.

Titration of thallium was made as follows: Twenty five milliliters of a standardized thallous perchlorate solution were pipetted into a titration cell. To this were added five milliliters of 1 VF sodium bromide, five milliliters of 9 VF perchloric acid and five milliliters of water. In the case of titration with chlorine, five milliliters of 8 VF hydrochloric acid and ten milliliters of water were added. The generator current was adjusted and the titration was begun. When the approximate time for the titration was known, the generation was continued to within a few seconds of the end point. The generation was then continued in short intervals and the indicator current noted at each pause. A plot of the indicator current vs. generation time was constructed from the data and the linear portion of this plot was extrapolated to zero indicator current. The intercept was designated as the titration time. The blank time was subtracted from the titration time to give the corrected titration time. The corresponding weight of thallium was calculated from the values of the corrected titration time and the rate of generation.

The sensitivity of the indicator electrodes was maintained by shorting them to the generator anode after each blank and every titration and generating bromine or chlorine for 50 seconds at the high rate. This solution was removed

and the electrodes were rinsed with water. The electrodes were stored in 1 VF hydrochloric acid when they were not in use.

Discussion of the Method

Indicator Current Behavior - A plot of the indicator current against time of generation when titrating thallium(I) in either perchloric acid-sodium bromide or hydrochloric acid solutions shows a small residual indicator current before generation is begun, a current increase to a flat maximum, a minimum at the equivalence point for the oxidation of Tl (I) to Tl (III) and finally a current increase. When the indicator potential is applied there is an initial surge of indicator current (to nearly 40 microamperes). The current then drops off to a small residual value of one to three microamperes. When titrating in the perchloric acid-sodium bromide solution, there may be an initial indicator current of as much as five microamperes if the sample was acidified several minutes before titrating. It is believed that this current is due to bromine formed by air oxidation of the bromide in acid solution. The samples were ordinarily not acidified until immediately before they were to be titrated.

The initial rise, the flat maximum and the decrease of the indicator current observed prior to the time calculated for the complete oxidation of the thallium areattributed to the reversibility of the thallous-thallic half-cell at the indicator electrodes. Presumably the current is controlled during the initial linear rise by difussion of the Tl (III)

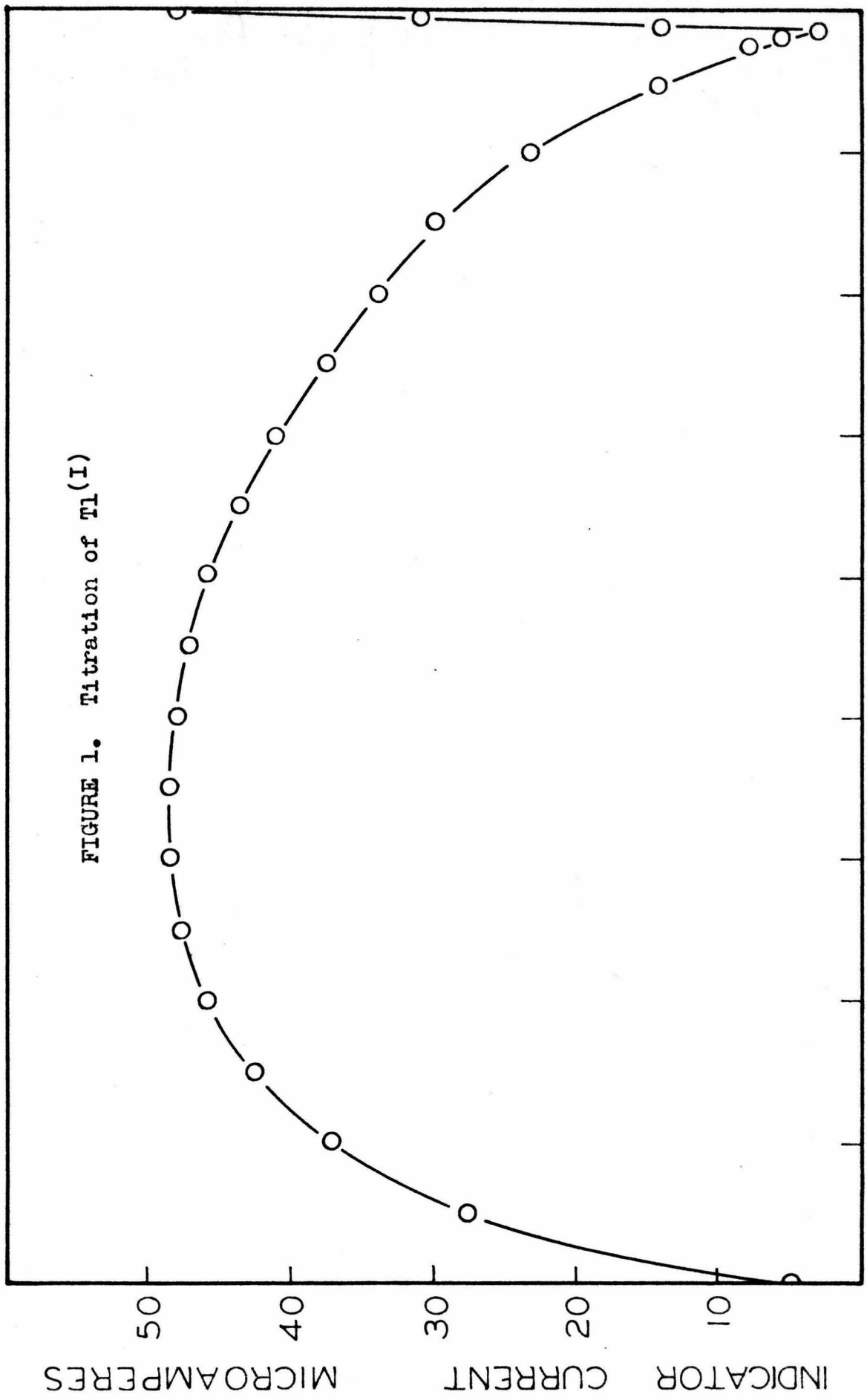

FIGURE 1. Titration of $T_1^{(I)}$

to the indicator cathode, and by diffusion of Tl (I) to the indicator anode during the linear current decrease before the equivalence point. The broad maximum occurs near to the calculated time for equal concentrations of Tl (I) and Tl (III). However, the point of maximum indicator current would not be expected to occur precisely at the time corresponding to equal concentrations unless the diffusion coefficients for both the thallous and the thallic species were the same and the indicator electrodes were the same size.

In the vicinity of the equivalence point, the concentrations of Tl (I) and bromine are very small, after the equivalence point, the bromine concentration increases and its diffusion to the indicator cathode determines the magnitude of the indicator current.

Titration of Tl (I) with Bromine and with Chlorine

The standard potential of the thallous-thallic couple[4],

$$Tl^{+} \rightleftharpoons Tl^{+++} + 2\bar{e} \qquad E_o = -1.25 \text{ volts}$$

in a non-complexing medium such as perchloric acid appears to be too great for a method based upon the oxidation of Tl (I) with either chlorine or bromine. The stability of both the bromide and chloride complexes of Tl (III) makes the formal potential more positive in bromide or chloride solutions (-0.78 volts in hydrochloric acid)[3] so that the titration of Tl (I) with bromine or chlorine in solutions

of the halides is possible. The formal potential calculated in bromide solutions from the data of Benoit[1] on the dissociation constants of the thallic bromide complexes is slightly more positive than that given above for chloride solutions. In the procedure described here, there is apparently no advantage in titrating with chlorine rather than bromine.

Table I. shows the data obtained from confirmatory titrations which were carried out as described above. In solutions two formal in acid containing bromide or chloride, Tl (I) can be titrated in quantities ranging from 93 micrograms to 200 micrograms with a maximum deviation from the mean of about ± 0.8 micrograms. Samples as small as 93 micrograms can be determined with an accuracy of 0.2%. For quantities from 200 micrograms to 1900 micrograms, the determination is accurate to 0.1%.

It is thought that the factors limiting the accuracy of these titrations are the preparation and dilution of the standard solutions, the determination of the end point and the preparation of pure intermediate reagents. The accuracy with which the generator current could be determined was about 0.03%.

Comparison of the Coulometric Titration with other Methods

C. W. Sill and H. E. Peterson[9] determined thallium by a titration with standard 0.001 N sodium thiosulfate of the iodine liberated when an excess of potassium iodide solution was added to the thallium sample. The sample had been

treated initially with bromine to insure complete oxidation of the thallium to Tl (III) and the excess bromine removed with phenol.

Samples as small as 40 micrograms were determined with an accuracy of 2.5%. Samples of from 1000 to 5000 micrograms were determined with an accuracy of 0.2 to 0.3% if the solutions were treated in the dark; in daylight the errors were larger.

In a similar method, proposed by P.A. Shaw[8], the iodine formed by the reaction of Tl (III) and iodide was extracted with carbon disulfide and determined colorimetrically. The smallest samples studied were 500 micrograms and these could be determined with an accuracy of 3 to 5%.

TABLE I

Confirmatory Titrations

Titration With Bromine

Thallium, micrograms

Taken	Found	Error	Percent Error
1873.7[a]	1875.9	+ 2.2	+ 0.12
	1875.3	+ 1.6	+ 0.09
	1871.6	- 2.1	- 0.11
	1873.2	- 0.5	- 0.03
	1873.7	0.0	0.00
	1874.9	+ 1.2	+ 0.06
Average	1874.1	+ 0.4	+ 0.02
1555.1[a]	1555.0	- 0.1	- 0.05
	1555.7	+ 0.6	+ 0.03
	1555.0	- 0.1	- 0.05
Average	1555.2	+ 0.1	0.00
935.9[a]	935.2	- 0.7	- 0.07
	936.1	+ 0.2	+ 0.02
	938.7	+ 2.8	+ 0.30
	935.2	- 0.7	- 0.07
	936.9	+ 1.0	+ 0.11
	935.6	- 0.3	- 0.03
	935.2	- 0.7	- 0.07
Average	936.1	+ 0.2	+ 0.02

TABLE I (continued)

Confirmatory Titrations

Titration With Bromine

Thallium, micrograms

Taken	Found	Error	Percent Error
187.4[b]	186.6	- 0.8	- 0.42
	187.9	+ 0.5	+ 0.27
	187.7	+ 0.3	+ 0.16
	188.2	+ 0.8	+ 0.42
	187.0	- 0.4	- 0.21
	187.0	- 0.4	- 0.21
Average	187.4	0.0	0.00
93.59[b]	93.50	+ 0.09	+ 0.10
	93.55	+ 0.04	+ 0.04
	93.60	+ 0.01	+ 0.01
	92.86	- 0.73	- 0.78
	93.70	+ 0.11	+ 0.12
Average	93.44	+ 0.15	+ 0.16

a. High generation Rate 1.0385×10^{-7} equivalents/sec.

b. Low gneration Rate 1.0393×10^{-8} equivalents/sec.

TABLE II

Confirmatory Titrations

Titrations With Chlorine

Thallium, micrograms

Taken	Found	Error	Percent Error
1873.7[a]	1870.3	- 3.4	- 0.18
	1870.5	- 3.2	- 0.17
	1876.4	+ 2.7	+ 0.14
	1872.6	- 1.1	- 0.06
	1878.5	+ 4.8	+ 0.25
Average	1873.6	+ 0.1	0.00
1555.1[a]	1556.7	+ 1.6	+ 0.09
	1555.2	+ 0.1	0.00
	1556.2	+ 1.1	+ 0.06
	1553.0	- 2.1	- 0.11
Average	1555.3	+ 0.2	+ 0.01
935.9[a]	930.8	- 5.1	- 0.55
	936.1	+ 0.2	+ 0.02
	944.0	+ 8.1	+ 0.86
	936.3	+ 0.4	+ 0.04
	935.9	0.0	0.00
	936.6	+ 0.7	+ 0.07
Average	936.6	+ 0.7	+ 0.07

TABLE II (continued)

Confirmatory Titrations

Titrations With Chlorine

Thallium, micrograms

Taken	Found	Error	Percent Error
187.4[b]	187.3	- 0.1	- 0.05
	187.8	+ 0.4	+ 0.21
	187.5	+ 0.1	+ 0.05
	187.3	- 0.1	- 0.05
	186.8	- 0.6	- 0.32
	187.1	- 0.3	- 0.16
Average	187.3	- 0.1	- 0.05
93.59[b]	93.92	+ 0.33	+ 0.35
	93.61	+ 0.02	+ 0.02
	93.71	+ 0.12	+ 0.13
	93.61	+ 0.02	+ 0.02
	92.87	- 0.28	- 0.30
	92.87	- 0.28	- 0.30
Average	93.43	- 0.16	- 0.17

a. High Generation Rate 1.0385×10^{-7} equivalents/sec.

b. Low Generation Rate 1.0393×10^{-8} equivalents/sec.

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PART II

THE COULOMETRIC TITRATION OF ANILINE BY MEANS OF ELECTROLYTICALLY GENERATED BROMINE AND CUPROUS COPPER AND AN AMPEROMETRIC END-POINT

THE COULOMETRIC TITRATION OF ANILINE BY MEANS OF ELECTROLYTICALLY GENERATED BROMINE AND CUPROUS COPPER AND AN AMPEROMETRIC END-POINT

Electrolytically generated bromine has been used as an intermediate oxidizing agent in secondary coulometric processes by Sease, Niemann and Swift[1], Myers and Swift[2], Brown and Swift[3] and Wooster, Farrington and Swift[4]. This process, combined with an amperometric end-point, has been used for the determination of reducing agents such as thiodiglycol, tripositive arsenic, tripositive antimony and iodide. Also, in an extension of these processes to the determination of oxidizing agents, electrolytically generated cuprous copper has been used as a reducing intermediate in a secondary coulometric titration of chromate and vanadate[5].

In these procedures, the substance to be determined reacts with the electrolytically generated intermediate, which is produced in the solution by the passage of a known constant current for a measured time. The end-point is obtained by observing the current flow between two platinum indicator electrodes which have a small potential difference impressed upon them.

The qualifications which the intermediate half-cell must possess are discussed by Meier, Myers and Swift[5]. Briefly, there must exist conditions such that the reactive form of the half cell is capable of being produced electrolytically in the solution with 100 percent current efficiency,

and this active constituent must react rapidly and stoichiometrically with the substance to be determined. If the amperometric end-point is to be used any excess of the active species must cause a current between the two indicator electrodes which is directly proportional to the concentration of the excess agent.

In general, the substances which have been titrated have reacted rapidly and stoichiometrically with the electrolytically generated intermediate -- at least, the reaction rate has been more rapid under these conditions than the generation rate. If the reaction between the electrolytically generated constituent and the substance being titrated is not as rapid as the generation rate, the indicator current will increase prematurely during the titration, making the determination of the end-point difficult.

In the course of an investigation of the bromination of organic compounds in aqueous solution, it was found that the rate of substitution of bromine in certain aromatic compounds was slow, and the end-point determination therefore difficult. Inasmuch as the secondary coulometric process with an amperometric end-point possesses certain advantages, further investigation of its applicability to such titrations seemed desirable.

In conventional volumetric procedures, such titrations are usually carried out by the addition of an excess of bromine followed after an appropriate time by a back titration.

In order to adapt such a bromometric titration to the coulometric method, a means for the determination of the excess bromine must be found. Direct cathodic reduction of the bromine is not possible; the concentration of excess bromine is too small for reduction with 100% current efficiency. Since the cuprous-cupric copper couple has been found to possess the qualifications for a coulometric intermediate, the use of cupric-copper and bromide as dual intermediates was investigated. The titration was carried out by generating an excess of bromine, permitting it to react for the necessary time, then back titrating the excess with electrolytically generated cuprous-copper.

This paper describes the use of these intermediates for the determination of aniline.

Experimental

Chemicals - All chemicals were reagent grade.

The stock aniline solution was prepared by dissolving freshly distilled aniline in 0.02 VF (volume formal) hydrochloric acid. Air was removed by bubbling nitrogen through the solution to prevent oxidation and decomposition of the aniline. This stock solution was standardized by a modification of the bromometric method as follows: Ten milliliter samples of the stock aniline solution were weighed into five hundred milliliter conical flasks containing one hundred milliliters of boiled, distilled water, two grams of potassium bromide and five milliliters of 6 VF

hydrochloric acid. About twenty five milliliters of standard 0.02790 VF potassium bromate solution were weighed into the solution and allowed to react for about three minutes in the closed vessel; two grams of potassium iodide were added and the iodine titrated with standard sodium thiosulfate to a starch end-point. The standardization gave 1.415×10^{-4} equiv. of aniline per gram of solution with a mean deviation of 0.2 percent.

The potassium bromate solution was standardized iodometrically by weight titration against standard thiosulfate. The thiosulfate solution was standardized by weight titration against a standard potassium iodate solution.

Separate cupric copper and bromide solutions were prepared. 0.2 VF solution of copper sulfate in 12 VF hydrochloric acid was prepared from twice recrystallized copper sulfate. Previously, the 12 VF hydrochloric acid had been found by electrolytic oxidation with bromine to contain approximately 1×10^{-6} equivalents of reducing material in a ten milliliter sample; this effect was eliminated by the addition of the required amount of a saturated solution of chlorine in hydrochloric acid. One volume formal sodium bromide solutions were used. No extraneous oxidizing or reducing materials were found in these solutions.

The laboratory distilled water was boiled to eliminate an oxidizing agent, presumed to be chlorine.

Apparatus - The apparatus used was essentially the same as that described by Meier, Myers and Swift[5] with the modifications described by Ramsey, Farrington and Swift[6].

Preliminary Adjustments - The current in the generator circuit was determined as described in Reference (5) and corresponded to 1.0375×10^{-7} equivalents per second. A potential of 200 mv. was impressed upon the indicator electrodes.

When the coulometric apparatus was not in use, the electrodes were shorted to the generator anode and stored in a solution approximately 2 VF in hydrochloric acid. Immediately before each set of titrations, the electrodes were placed in a solution 0.1 VF in sodium bromide and 1 VF hydrochloric acid contained in a titration cell (a 40 x 80 mm weighing bottle), and bromine was generated in the solution for thirty seconds at high rate. This procedure aided in maintaining the stability of the electrode sensitivity; treatment with cleaning solution was only occasionally necessary.

Procedure - In carrying out a titration, twenty-five milliliters of a solution prepared by dilution of the stock aniline solution were pipetted into a titration cell; five milliliters of the 0.2 VF copper sulfate solution (12 F in HCl), five milliliters of the 1 VF sodium bromide solution and ten milliliters of water were added. The generator current was set at the desired value and the initial indicator current was observed.

When analyzing an unknown aniline solution, trial titrations were made by generating bromine for a period of time, stopping the generation and observing the change of the indicator current with time. For titrations of greater than 100 seconds generation time, it was most convenient to generate bromine in the solution at the high rate (10^{-7} eq./sec.) until the indicator current was "off scale" with the indicator current microammeter shunted down to one-third of its normal sensitivity. After stopping the generation, a pause of about thirty seconds was often necessary before the indicator current was again "on scale". In the determination of smaller samples, generation of bromine in ten second intervals, followed by a pause to observe the change of the indicator current was found to be successful.

If the equivalence point for the formation of tribromoaniline had not been reached, the indicator current decreased with time during this pause showing that the bromine was still reacting with the aniline. However, as the equivalence point was approached, the rate of decrease became slower. If the equivalence point were passed, the indicator current did not decrease noticeably during the thirty second wait.

When the approximate equivalence point was known, the indicator circuit was opened during the titration and generation of bromine was continued until a twenty five second excess was produced at the high generation rate. This quantity was found to be sufficient to bring the reaction to

completion in one minute. Then the polarity of the internal generator electrode was reversed and cuprous copper was generated until most of the excess bromine had been reduced as demonstrated by the return of the indicator current to the scale. The generation was continued in half second intervals until the indicator current decreased to fifteen microamperes. Between each period of generation a ten second pause was taken while the indicator current reached a steady value.

A plot of indicator current against time of generation showed a rise in the current initially, followed by an "off scale" period, then with generation of cuprous copper a return to "on scale", followed by a linear decrease in the indicator current during the range of 40 to 10 microamperes. A correction for the impurities in the reagents used and any possible loss of bromine, was made by titrating six blank solutions containing five milliliters of 0.2 VF copper sulfate in 12 VF hydrochloric acid, five milliliters of 1 VF sodium bromide and thirty-five milliliters of water. The generator current was set at the desired value and bromine was generated for twenty-five seconds, the time of generation of excess bromine in an aniline titration. The solution was permitted to stand for one minute without stirring. The polarity of the internal generator electrode was reversed and cuprous copper was generated until an indicator current of fifteen microamperes was obtained.

The "correction time" was designated as the difference

between two times: the larger time was the period of bromine generation and the shorter time was that time of copper generation back to the arbitrary value fifteen microamperes. The average "correction time" was determined from the last four blanks which were usually the most consistent.

The time of cuprous copper generation back to an indicator current of fifteen microamperes for the aniline titration and the "correction time" were subtracted from the total time of bromine generation to obtain the corrected titration time. The corresponding weights of aniline were calculated from the titration time and the rate of generation.

If the generation of cuprous copper was continued beyond the time corresponding to an indicator current of fifteen microamperes, the indicator current passes through a broad minimum, and again increased as cuprous copper was generated in excess. The arbitrary value of fifteen microamperes on the linear portion of the curve was chosen as the end-point for both the titration and the blank rather than the time corresponding to the minimum.

This end-point was found to be stable and reproducable. By controlling the polarity of the internal generator electrode, one could generate bromine or cuprous copper as desired and so pass through this arbitrary point, as well as the minimum, several times without marked error. A series of experiments showed that one could pass through the minimum five times before the time corresponding to fifteen microamperes of indicator current varied over one-tenth of a second.

Discussion of the Method

The Bromine-aniline Reaction - Pamfilov[7] states in his review of methods for the quantitative determination of aniline that the bromometric method is the most convenient and accurate one for concentrations in the range 0.1 VF to 10^{-5} VF. This method is based upon the fact that the reaction of bromine and aniline to yield 2,4,6 tribromoaniline can be made quantitative and rapid. Later, Pamfilov and Kisselva[8] showed in a study of the bromometric method (with use being made of a potentiometric end-point) that the reaction is rapid only when the bromination is done in "weakly" acid solutions. In 0.1 VF hydrochloric acid, the reaction is so slow that a direct titration with bromine is very difficult.

There would be an advantage in adapting the bromometric method to solutions of higher acid concentrations because aniline is conveniently collected in acid solutions. Therefore experiments were made to study the application of a coulometric process with an amperometric end-point to the determination of aniline in acid solutions. It was observed that in solutions approximately 10^{-5} VF in aniline and 1 VF in hydrochloric acid, the bromination reaction was so slow that bromine accumulated in the solution during the titration; thus after four seconds of continuous high rate generation, the indicator current was "off scale" and when the

end-point was reached there was no characteristic increase in the indicator current.

A satisfactory procedure required the generation of an excess of bromine sufficient to complete the reaction in a short time and experiments showed that at least twenty five seconds of excess bromine was necessary for completion of the reaction in one minute. This excess represents only 25×10^{-7} equivalents, which is a quantity too small for determination by a direct cathodic reduction since the diffusion of bromine to the cathode surface would be so slow that 100 percent current efficiency could not be achieved. Therefore use was made of the generation of cuprous copper.

The Required Excess of Bromine - The concentration of excess bromine had to be sufficient to cause completion of the reaction in a reasonable time, yet the excess could not be such as to cause significant loss of bromine through volatilization during the time allowed for the completion of the reaction. Experiments showed bromine equivalent to twenty five seconds of generation (with a current of approximately 10 milliamperes) were required for completion of the reaction in one minute. Less generation of excess bromine caused incomplete reaction and low results; a five second excess led to an error of several percent. Although the apparatus provided for low rate generation at about one-tenth the rate used above, a 250 second excess of bromine was then necessary which made the titration inconvenient.

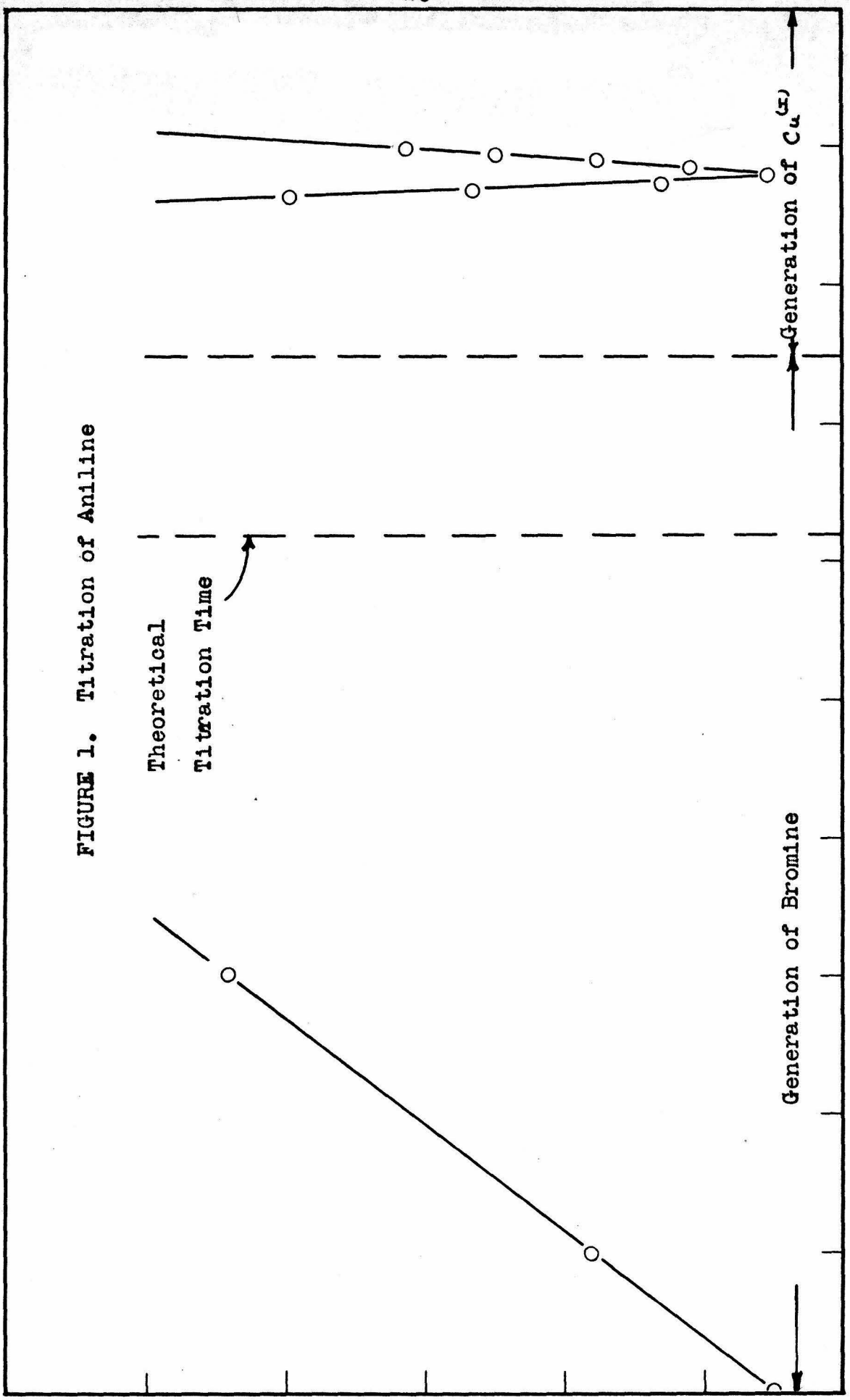

FIGURE 1. Titration of Aniline

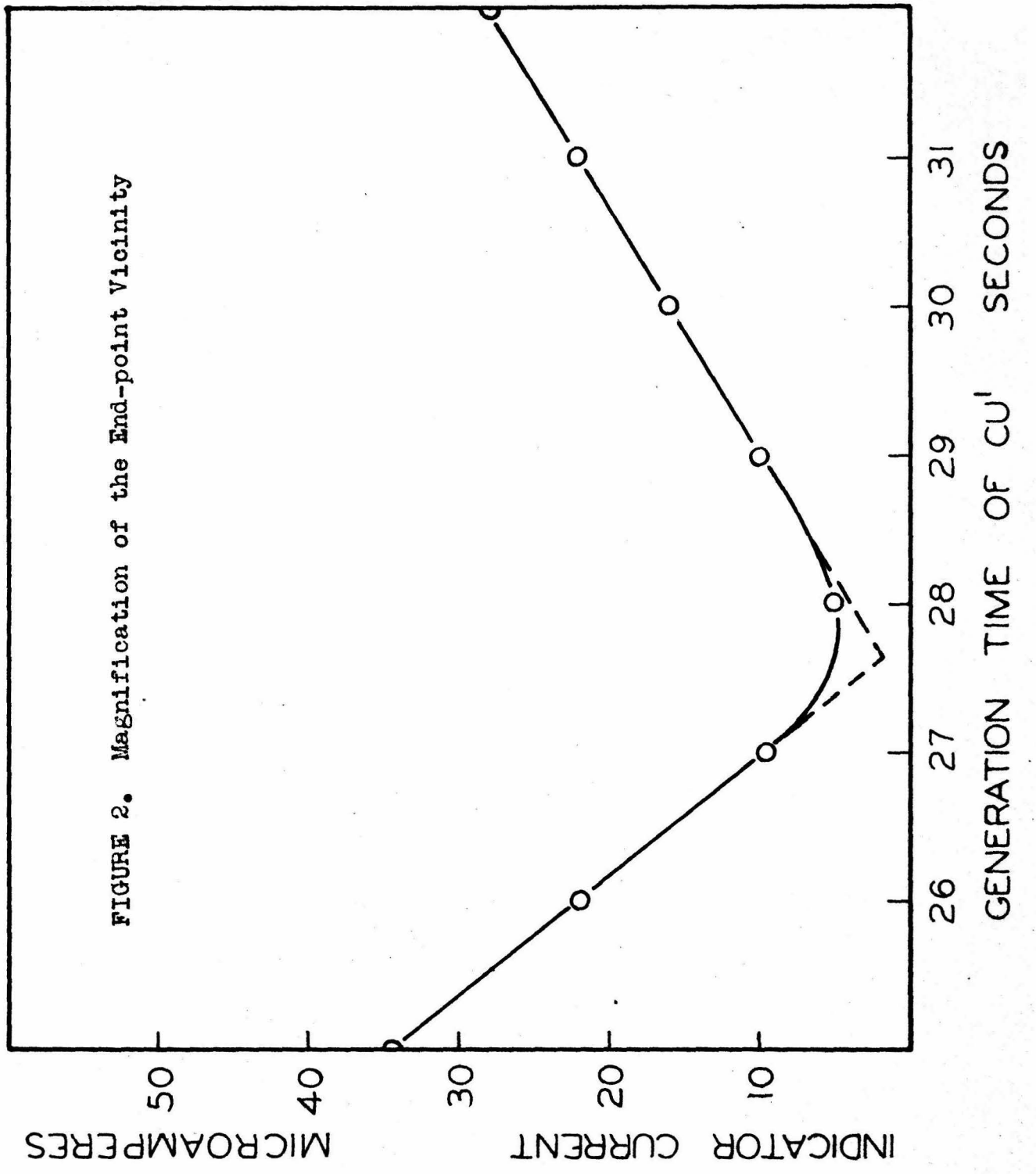

FIGURE 2. Magnification of the End-point Vicinity

Titration in Acetic Acid-acetate Solutions - Pamfilov and Kisselva[8] state that the rate of reaction is dependent upon the pH of the solution. The reaction is slower in acid solution and the rate increases with pH. At pH 0 - 1, the rate is retarded enough that the dual intermediate must be used. Experiments have shown that in an acetate buffer, pH 4.5, the rate of the reaction is sufficiently rapid that a secondary coulometric titration with an amperometric end-point using only bromine can be performed. For pH values greater than five, the amperometric end-point cannot be used, because the hydrolysis of the bromine causes late end-points and correspondingly high results. Data showing the effect of pH on the detection of bromine in bromide solutions by means of an amperometric end-point are given in Part III.

Confirmatory Titrations - Table I contains data obtained from confirmatory titrations carried out as described in the procedure above. The titrations contained in the table show errors of less than 0.4 percent for samples between 100 and 300 micrograms, and consistently less than 1.5 percent for samples between 10 and 100 micrograms.

The factors limiting the accuracy of the above measurements are thought to be: the preparation and standardization of solutions, the instability of the aniline solutions and the dilution of the stock aniline solution. In the larger samples, there was considerably better agreement among titrations within one group than between the average titer of the group and the calculated value for the titer.

The average "correction time" was 0.3 second of generation time.

Acknowledgment - The author wishes to thank Professor Howard J. Lucas for making available the sample of redistilled aniline.

TABLE I

CONFIRMATORY ANALYSES

Aniline (micrograms)

Number	Taken		Found	Error	% Error
I	274.1		275.1	1.0	0.36
			275.4	1.3	0.47
			275.7	1.6	0.58
			275.1	1.0	0.36
			275.0	0.9	0.33
			274.9	0.8	0.29
		Average	275.2	1.1	0.40
II	199.5		199.6	0.1	0.05
			199.4	-0.1	-0.05
			200.1	0.6	0.30
			199.5	0.0	0.00
			199.5	0.0	0.00
			200.1	0.6	0.30
		Average	199.7	0.2	0.10
III	99.7		100.1	0.4	0.40
			99.1	-0.6	-0.60
			99.8	0.1	0.10
			99.8	0.1	0.10
			99.6	-0.1	-0.10
			99.0	-0.7	-0.70
			99.4	-0.3	-0.30
			99.5	-0.2	-0.20
		Average	99.55	-0.15	-0.15

TABLE I (Continued)

CONFIRMATORY ANALYSES

Aniline (micrograms)

Number	Taken		Found	Error	% Error
IV	52.2		52.8	0.6	1.15
			52.2	0.0	0.00
			52.2	0.0	0.00
			51.7	-0.5	-0.96
			51.8	-0.4	-0.77
			51.9	-0.3	-0.57
		Average	52.1	-0.1	-0.19
V	26.1		26.1	0.0	0.00
			26.0	-0.1	-0.38
			26.1	0.0	0.00
			26.1	0.0	0.00
			25.7	-0.4	-1.5
		Average	26.0	-0.1	-0.38
VI	13.0		12.5	-0.5	-3.8
			13.0	0.0	0.0
			13.0	0.0	0.0
			12.9	-0.1	-0.8
			12.8	-0.2	-1.5
		Average	12.8	-0.2	-1.5

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PART III

STUDIES OF THE BROMINE-CONTROLLED DIFFUSION CURRENT

STUDIES OF THE BROMINE-CONTROLLED DIFFUSION CURRENT*

The secondary type of coulometric process involves an intermediate half-cell reaction which is caused to take place with 100% current efficiency at the generating electrodes. Meier, Myers and Swift[2] have discussed the advantages of this type of process and the characteristics of suitable intermediate half-cell reactions.

Bromine is one such intermediate which has been sucessfully employed for the titration of reducing agents[1,3,4,5]. The bromine is generated electrolytically in 0.1 VF (volume formal) solutions of sodium bromide and acid and reacts with the reducing agent. When the titration is completed, bromine is generated in excess and an indicator current flows between two smooth platinum indicator electrodes (2.1 x 2.4 cm) which have a small potential impressed on them. When the bromide concentration is much greater than the bromine concentration, the current is limited by the diffusion of bromine and is proportional to the concentration of the bromine. This condition is satisfied after the end point of a titration; the bromide ion concentration is 0.1 VF and the bromine concentration is about 10^{-5} VF. The phenomenon provides a sensitive end-point device for coulometric titrations with bromine.

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* Part of this work was done as Senior Research, Chemistry 80.

It was the purpose of these experiments to study the bromine-bromide diffusion current, the effects of the concentration of bromine, bromide and hydrogen ion; the minimum bromide ion concentration necessary to maintain generation of bromine with 100% current efficiency was determined.

Experimental

Chemicals

All chemicals were "reagent" grade.

One volume formal sodium bromide solutions were prepared from the salt.

60% Perchloric acid (9 VF) was tested for reducing agents. Only very small amounts were detected and were determined by titration of blank solutions.

Standard solutions of tripositive arsenic were prepared from Bureau of Standards arsenious oxide and were diluted to appropriate volumes to provide standard solutions for analysis.

A 0.002 VF solution of potassium permanganate was prepared.

Buffer solutions corresponding to pH values of 4, 5, 6 and 7 were prepared. Those at pH 4 and pH 5 were prepared from acetic acid and sodium acetate and those at pH 6 and pH 7 from sodium dihydrogen phosphate and sodium monohydrogen phosphate. The total concentration of solute in each was 0.1 VF.

Boiled distilled water was used for all solutions.

Apparatus

The apparatus was the same as that described by Meier,

Myers and Swift[2] with the following changes: In place of the laboratory direct current supply, a simple voltage-regulated rectifier was used, which was connected to the alternating current line through a voltage-regulating Sola transformer. The generator cathode was enclosed in a shield rather than the generator anode.

Preliminary Adjustments

The generator current was determined by measuring the voltage drop across a standardized 199.87 ohm resistance through which the current was passing. Generation rates of 1.0386×10^{-8} and 1.0385×10^{-7} equivalents per second were used. When not in use, the indicator electrodes were shorted together and stored in a solution about 0.1 VF in perchloric acid. A similar solution of perchloric acid was placed in the generator cathode shield.

Before each set of titrations, the indicator electrodes were shorted together and connected to the generator anode; bromine was generated at the high rate for about thirty seconds. This procedure was repeated after each blank or titration to maintain the indicator electrode sensitivity.

Procedure

The minimum bromide concentration necessary to permit the generation of bromine with 100% current efficiency was determined from a series of titrations of arsenious acid with

decreasing bromide concentrations. All titrated solutions had a total volume of 40 milliliters and contained 2.5 milliliters of 9 VF perchloric acid and 25 milliliters of dilute standard arsenious acid. Dilute solutions of sodium bromide were added to give bromide concentrations of 0.2, 0.1, 0.05, 0.025, 0.01, 0.0075 and 0.005 VF.

As soon as the titration cell (a 40 x 80 mm weighing bottle) was attached to the stirring apparatus, generation of bromine was started. The indicator potential was set at 200 millivolts. By means of the built in potentiometer, the generator current was checked during the course of the titration and the current was held constant by making small adjustments. When the end-point was reached as indicated by the rapid rise of the indicator current, generation was continued in half second intervals; readings of the current were taken at each interval. A plot of the indicator current against the generation time (described by Myers and Swift[3]) was constructed and the linear portion was extrapolated to zero indicator current; the intercept on the time axis was designated as the generation time of the sample.

A correction for reducing impurities in the reagents was made by generating in a blank solution of the composition of the sample with the substitution of 25 milliliters of water for the arsenite solution. The generation was done in half-second intervals and a plot of the indicator current vs. time was made. The blank solution generation time was subtracted from the generation time of the sample to give the corrected titration time.

When the bromide concentration was small enough that 100% current effeciency was not achieved at the generator anode, high values were obtained for the corrected titration time.

In studying the effect of pH on the end-point indicator current, samples containing 10 milliliters of standard arsenite solutions, 5 milliliters of 1 VF sodium bromide solution and 25 milliliters of buffer solution were titrated as described above. Blank solutions containing 10 milliliters of water in place of the arsenite were also titrated.

Preliminary observations of the maximum pH permissible were rapidly obtained from these blank solutions. In the absence of enough acid, the indicator current failed to rise when excess bromine was generated because of the rapid hydrolysis of the bromine. When it was believed that a maximum pH was found, a confirmatory test was made by the addition of 5 milliliters of 9 VF perchloric acid to the blank. The hydrolyzed bromine rapidly reverted to bromine and a sudden rise of the indicator current "off scale" was observed.

It was of interest for the understanding of the bromine-bromide-controlled diffusion current to observe the indicator currents in solutions containing concentrations of bromine and bromide ranging from pure bromide to essentially pure bromine. A curve showing such an indicator current was obtained by placing a titration cell containing a solution of sodium bromide in perchloric acid on the stirring apparatus,

adding dilute permanganate from a burette and observing the current flow between the indicator electrodes as the bromide was oxidized to bromine. The permanganate and its reduced form, $Mn^{(II)}$, did not give an indicator current.

Discussion

Effect of Bromide Concentration on Coulometric Titrations With Bromine

The minimum bromide concentration permissible in a coulometric titration with an amperometric end-point could be fixed by either of two factors; there is a critical concentration of bromide below which the oxidation of bromide at the generator anode does not take place with 100% current efficiency, and a minimum concentration below which the indicator current will not be limited by the diffusion of bromine and will not be linearly proportional to the bromine concentration. Experiments have indicated that the limitation on the bromide concentration imposed by the requirement that the oxidation of the bromide take place with 100% current efficiency is the dominant one. At bromide concentrations too small to achieve 100% current efficiency, the indicator current is still sensitive to and proportional to the bromine concentration. With these small bromide concentrations, the sensitivity of the indicator system toward bromine is decreased; that is, the increase of indicator current per unit increase of bromine concentration is smaller in more dilute bromide concentrations.

Table I shows the corrected titration times for a single

TABLE I

Sample: Arsenious acid
Sodium Bromide
Perchloric acid 0.56 VF

Solution Volume: 40 milliliters

Generation rate: 1.0385×10^{-7} equivalents per second

Theoretical Titration time: 124.2 seconds

Current Density: 40 milliamperes per square centimeter

Corrected Titration Time	Bromide Concentration
124.3 seconds	0.24 VF
124.3	0.24
124.2	0.24
124.2	0.025
124.1	0.025
124.2	0.025
124.3	0.025
124.3	0.010
124.3	0.010
124.2	0.010
124.2	0.010
130.0	0.0075
128.4	0.0075
127.8	0.0075
173.0	0.0050
157.0	0.0050
163.0	0.0050

arsenious acid sample titrated with bromine at a series of bromide concentrations. It has been concluded that 0.010 VF bromide is the minimum concentration permissible under the conditions of the experiment (a maximum current density of 40 milliamperes per square centimeter).

Effect of pH on the Indicator Current

Since bromine is known to hydrolyze appreciably in even slightly acid solutions, it was desirable to determine the maximum pH at which a stable indicator current could be obtained, when the bromide concentration was 0.1 VF.

In a blank solution containing 25 milliliters of pH 6 buffer, 5 milliliters of 1 VF sodium bromide and 10 milliliters of water, less than one microampere indicator current was observed when bromine was generated at low rate until 65 seconds of generation were completed. The indicator current increased slowly to 4 microamperes at 100 seconds. When 5 milliliters of 9 VF perchloric acid were added to the blank after 100 seconds of generation, the current rose "off scale". The reducing impurities in the buffer solution were determined by titrating 25 milliliters of the buffer, 5 milliliters of 1 VF sodium bromide, 5 milliliters of 9 VF perchloric acid and 5 milliliters of water. The time of generation was only 9 seconds.

In a blank solution containing 25 milliliters of pH 5 buffer, 5 milliliters of 1 VF sodium bromide and 10 milliliters of water, an indicator current was obtained when bromine was

generated at low rate. The current showed adequate stability for quantitative measurements. When generation was stopped, the current dropped on the average one microampere in thirty seconds.

The corrected titration time for a solution containing 10 milliliters of arsenite solution, 25 milliliters of pH 5 buffer and 5 milliliters of sodium bromide agreed with the corrected time for the same size sample of arsenite titrated in 0.56 VF perchloric acid solution within 0.2 percent.

The indicator currents observed in the titrations of blanks and samples of arsenic at pH 4 showed no instability due to hydrolysis of the bromine. It was concluded that pH 5 was the maximum pH at which coulometric titrations with an amperometric end-point involving bromine could be used.

The Bromine-Bromide Diffusion Current

A 40 milliliter sample of sodium bromide (5.0×10^{-4} VF) containing 10 milliliters of 9 VF perchloric acid was attached to the stirring apparatus. A 0.002 VF solution of potassium permanganate was added dropwise to the stirred solution from a burette and the indicator current was observed following each addition. Initially, the pink color of the permanganate was discharged immediately, but as the titration proceeded, the time required for discharge of the color increased. Inasmuch as the rate of reaction between permanganate and bromide is appreciably slower as the bromide concentration is diminished, it was necessary to wait as much as two minutes between successive additions of the permanganate toward the end of the titrations.

The indicator current plotted against the volume of permanganate added is shown in Figure 1. The indicator current phenomena are best explained by means of diffusion processes occurring in the diffusion layers. In a rapidly stirred solution, thin stationary liquid layers next to the indicator electrode surfaces are postulated in which diffusion is the primary transfer process. Thus, with applied indicator potentials greater than that required to overcome the ohmic resistance of the solution, the rate of discharge of species at the indicator electrodes is dependent upon the rate of diffusion of the reacting solute from the bulk of the solution through the diffusion layer to the electrode surface. In rapidly stirred solutions, the diffusion layer is very thin and the rate of diffusion is proportional to the concentration gradient through the layer.

In solutions of bromine and bromide, the indicator electrode reactions are,

Anode $2Br^- - 2e^- \rightarrow Br_2$

Cathode $Br_2 + 2e^- \rightarrow 2Br^-$

No net reaction occurs at the indicator electrode surfaces. When the bromide concentration is large (0.1 VF) the current will be limited by the rate of diffusion of the bromine, which is observed to be linearly proportional to the bromine concentration. This fact is employed as a sensitive end-point method for coulometric titrations with bromine.

The curve obtained and shown in Figure 1.is interpreted as follows:

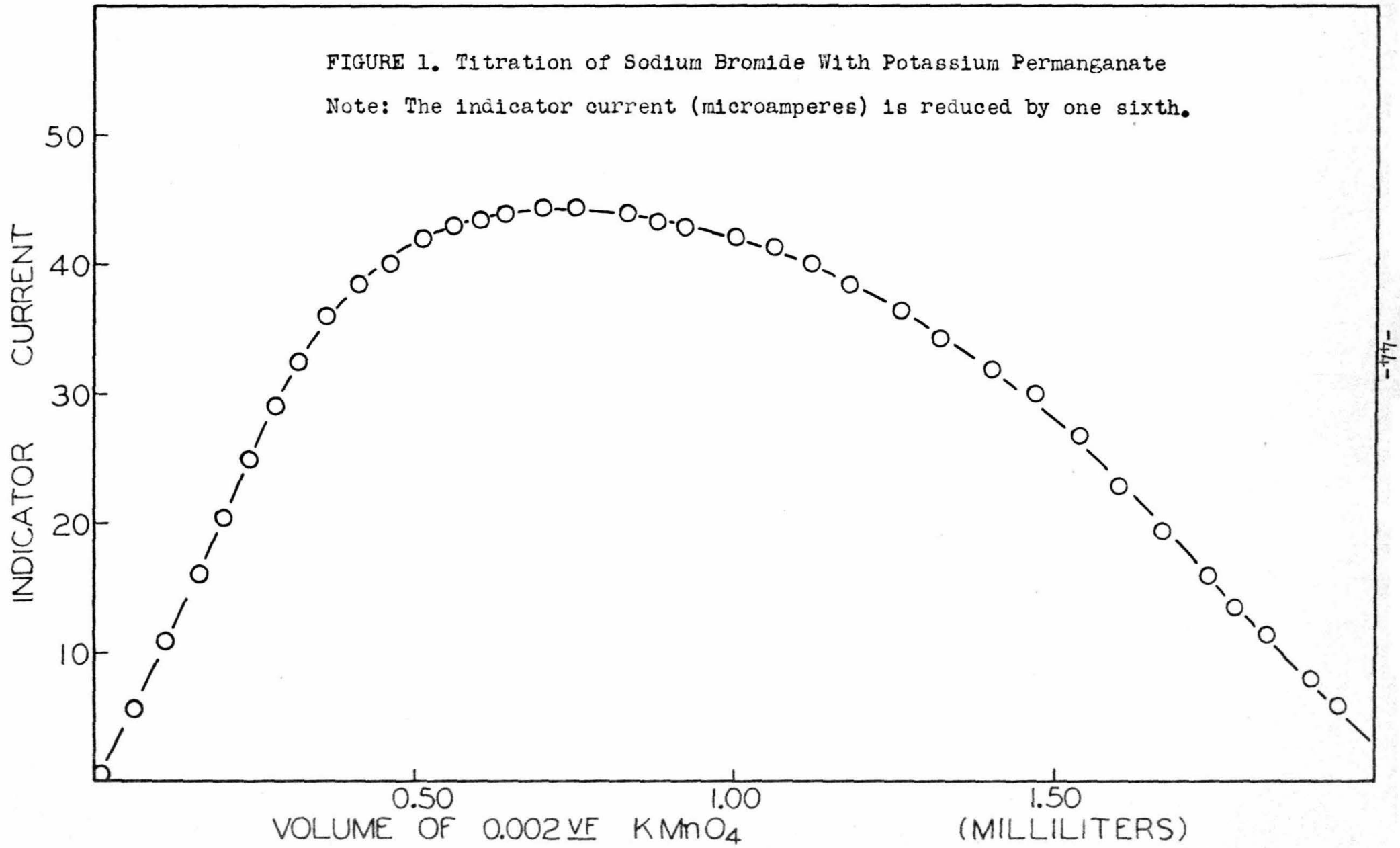
Initially, in the absence of bromine, the indicator current is zero, but the current increases rapidly as bromine is produced in the solution. When about one-third of the bromide is oxidized to bromine (the concentration of bromide is then four times that of the bromine) the indicator current becomes limited by the diffusion of the bromide and a maximum value of the indicator current is observed. Further oxidation of the bromide produces a decrease in the current.

The linear initial and final slopes of the curve and the location of the maximum depend upon the relative sizes of the electrodes and the diffusion coefficients of the reacting species. The smooth platinum indicator electrodes used in this study were the same size (2.1 x 2.4 cm.) so that it can be inferred that the diffusion coefficient of the bromine is greater than the coefficient of bromide.

The indicator current obtained in the titration of bromide with permanganate suggest this technique as a method for the determination of microgram quantities of bromide. The use of dilute permanganate solutions added from a microburette to a rapidly stirred perchloric acid solution of the bromide, with application of the bromine-bromide-controlled diffusion current for the detection of the end-point, need to be investigated and the accuracy determined. However, there is not sufficient time to study this proposed titration.

FIGURE 1. Titration of Sodium Bromide With Potassium Permanganate

Note: The indicator current (microamperes) is reduced by one sixth.



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PART IV

STUDIES OF HYDROGEN ION-CONTROLLED DIFFUSION CURRENTS BETWEEN PLATINIZED-PLATINUM ELECTRODES

STUDIES OF HYDROGEN ION-CONTROLLED DIFFUSION CURRENTS BETWEEN PLATINIZED-PLATINUM ELECTRODES

The determination of small quantities of strong acids in unbuffered solutions based upon the measurement of a hydrogen ion-controlled diffusion current was investigated by Ludwig Fresenius[3] as an application of the Nernst Diffusion Layer Theory[2,6,7]. He observed a current which was linearly proportional to the hydrogen ion concentration when a potential difference of the order of 150 millivolts was impressed upon two platinized-platinum electrodes immersed in a rapidly stirred solution which was saturated with hydrogen gas and was 0.1 VF (volume formal) in potassium chloride and 0.001 VF in hydrochloric acid.

Fresenius studied the effects of stirring, temperature, applied potential and electrode size and his results indicated that the phenomenon could be used as a method for the determination of small quantities of both strong and weak acids in aqueous solutions containing an inert supporting electrolyte. An electrode mechanism was proposed in terms of diffusion of hydrogen ions through the Nernst diffusion layer to a small platinized-platinum wire cathode and the diffusion of hydrogen gas to a larger platinized-platinum foil anode. The processes did not produce a net change in the hydrogen ion concentration of the solution and the applied potential was necessary only to overcome overvoltages and the resistance of the solution. The cathode was made of such size that the

current was limited by the rate of diffusion of the hydrogen ions to this electrode and therefore was proportional to the hydrogen ion concentration. At pH values of around 7 Fresenius observed a minimum in the current, and thereafter, with increasing pH the current increased.

At a fixed applied potential difference, the current increased linearly with the hydroxide ion concentration. However, the relative positions of the minimum of the curve and the neutral point depended upon the applied potential and on the electrode size.

The work of Fresenius indicated the possibility of making accurate measurements of hydrogen ion concentrations in the range between pH 3 and pH 11 in unbuffered solutions where the usual potentiometric methods are unreliable. Therefore, further investigations of the hydrogen ion-controlled diffusion current phenomena were carried out in order to evaluate application of the method to the end-point determination of coulometric titrations of acids by electrolytically generated hydroxyl ions. The results indicated the profitable use of this amperometric end-point in dilute unbuffered solutions in place of the potentiometric end-point. The accuracy of the method was established and an understanding of the electrode processes was gained.

As a part of these investigations, a study of the coulometric titration of hydrochloric acid was made and the results are presented.

Experimental

Chemicals

One formal solutions of potassium chloride for use as supporting electrolyte were prepared from "reagent grade" salt. These solutions were acidified with dilute hydrochloric acid to a pH of about four to minimize the effect of absorbed carbon dioxide and to provide sufficient acid to determine the blank solution titration time.

A one-tenth formal solution of hydrochloric acid was prepared from reagent grade acid and boiled distilled water. This solution was twice standardized against sodium carbonate during the study and was found to maintain a constant normality.

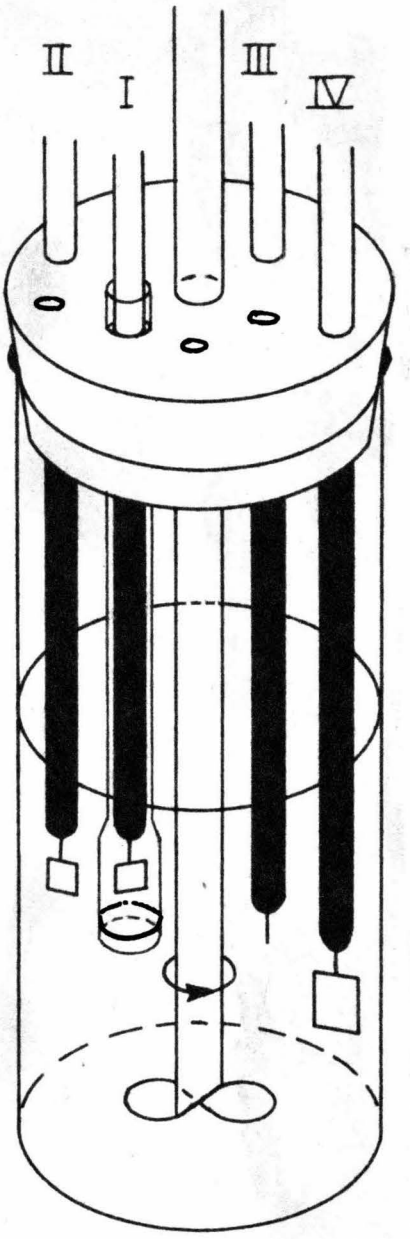
The laboratory distilled water was boiled to remove carbon dioxide and was stored in a container provided with a seal permitting removal of the liquid without the introduction of carbon dioxide.

A commercial hydrogen tank supplied the hydrogen gas. Small quantities of oxygen in the gas seemed to have no effect on the titrations.

Apparatus

The electrical circuit was essentially the same as that described by Meier, Myers and Swift[5] with a substitution for the laboratory direct current supply, of a simple voltage-regulated rectifier which was connected to the alternating current line through a voltage-regulating Sola transformer.

FIGURE 1.



I. Generator Cathode
0.5 x 0.5 cm.

II. Generator Anode
0.5 x 0.5 cm.

III. Indicator Cathode
0.02 cm. diameter
platinum wire,
0.1 cm. in length

IV. Indicator Anode
2.5 x 1.8 cm.

40 x 80 mm.
Weighing Bottle

TITRATION CELL

Figure 1. shows the titration cell used in the study. Under the conditions of the experiments, the relative positions of the indicator anode and cathode caused no significant difference in the sensitivity of the indicator system.

In Figure 1, the smooth platinum generator anode is enclosed in a shield consisting of a glass tube terminating in a sintered glass disc of "fine" porosity which isolates the anode from the body of the solution and prevents chlorine gas produced by the electrolysis from being swept into the solution. One formal potassium chloride was placed inside the shield. The level of the solution in the shield was maintained close to the level of the solution so that diffusion through the porous disc was minimized.

A simplified titration cell in which a 16 gage silver wire was substituted for the enclosed platinum anode avoided possible diffusion of chlorine into the solution. The silver chloride formed during the electrolysis adhered to the cathode and was removed from the surface by reversing the polarity of the generator electrodes and electrolyzing a solution 0.01 VF in sulfuric acid.

Inasmuch as the indicator current mechanism depends upon the presence of hydrogen gas in a solution, the titration cell provided for bubbling the gas through the solution. Carbon dioxide and dissolved oxygen were removed initially and an atmosphere of hydrogen provided above the solution during the titration.

A constant speed stirring motor of about 1650 r.p.m. was used.

The Electrode Systems

The generator electrodes were made from 0.003 in. platinum foil; the sizes are shown in Figure 1.

The indicator anode was made from 0.003 in. platinum foil; a 0.02 in. diameter platinum wire served as the indicator cathode. Both were carefully platinized to minimize overvoltages. The indicator electrodes were replatinized several times to aid in maintaining their sensitivity. The platinum foils were attached to fine platinum wires imbedded in 5 mm glass tubing filled with mercury. The electrodes could be easily disconnected from the titration cell.

The applied potential difference across the indicator electrodes could be varied from about zero to 300 millivolts. The effect of different applied potentials is discussed below. However, in the majority of titrations of the hydrochloric acid, the indicator potential was set at 150 millivolts.

The microammeter employed for observing the indicator current read fifty microamperes full scale at its normal sensitivity or 150 microamperes when it was shunted.

The indicator electrodes could be shorted together at will and initial polarization effects could be overcome rapidly if the indicator electrodes were momentarily shorted during the initial addition of the hydrogen gas.

The generator circuit was calibrated in the manner described by Meier, Myers and Swift[5]. The generation rate of 1.0385×10^{-7} equivalents per second was used in these studies. This rate was checked on several occasions and was observed to vary less than one-tenth of a percent.

Indicator Current Phenomena

It was observed by Fresenius[3] that a current flowed between platinized-platinum electrodes in a solution saturated with hydrogen gas containing hydrochloric acid and potassium chloride, 0.1 VF, when a potential difference less than that required for electrolysis was impressed across them. This current was proportional to the hydrogen ion concentration at pH values less than about 7.

An explanation of this observation requires a knowledge of the processes occurring at the electrode surfaces in a stirred solution. Agar[1] has pointed out that electrode processes depend upon the three methods by which the reacting solute can move from the bulk of the solution to the electrode surfaces: diffusion, convection (movement of the liquid containing the solute) and by ionic migration. Convection and migration do not account for the whole of the material reacting at the indicator electrodes so that a diffusion process to the electrode surface is necessary.

The theoretical interpretation usually applied to the diffusion current phenomena by Nernst[6] and Eucken[2] involves the hypothesis of a stationary layer of liquid in contact with the electrode. Within this layer diffusion of the solute to the surface of the electrode is the predominant

process. In stirred solutions, the thickness of the diffusion layer is small and the transport of the ions from the bulk of the solution to the electrode surface is therefore more rapid.

In the steady state, the concentration of the reacting solute at the interface must be less than that in the bulk of the solution; a concentration gradient exists throughout the diffusion layer. At the surface of the electrode, the concentration of the reacting substance is c_o while at a distance δ, the concentration is maintained at a constant value c_∞ by convection. The concentration gradient in the layer is linear and the diffusion current, j, per unit area is

$$j = \frac{D n_i F (c_\infty - c_o)}{\delta}$$

where D is the diffusion coefficient of the substance, n_i is the change of valence in the electrode reaction and F is the value of the Faraday. The thickness of the diffusion layer is assumed to be independent of the nature of the electrode process and of the character of the potential distribution. The value of δ depends upon the rate of stirring.

A refined treatment made by Levich[4] leads to a qualitative theory of the boundary layer for an electrode of arbi brary form, permits a velocity of liquid flow within the diffusion layer and accounts for both diffusion and convection effects.

The indicator current phenomena observed in these experiments can be interpreted in terms of the simple Nernst diffusion layer and adsorption of gases on the platinum electrodes. In a solution of pH less than 7 and which is 0.1 VF in potassium chloride, there is observed a surge of indicator current as the indicator potential difference is applied. At a potential difference of 150 millivolts, this surge is greater than fifty microamperes. Within ten seconds the current diminishes to about four microamperes. This surge involves certain initial electrode reactions followed by adsorption polarization and the establishment of a back e.m.f. which reduces the current flow.

At the indicator cathode,

$$2H^+ \rightarrow 2H - 2e^- \qquad 2H \rightarrow H_2$$

At the indicator anode,

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

The hydrogen and oxygen gases are adsorbed on their respective electrodes. During this step there is a surge of current. When the adsorption layer is produced the back e.m.f. produced at the electrodes by the adsorbed gases is sufficient to stop the passage of current between the electrodes.

When hydrogen gas is bubbled into the solution, there is an immediate current reversal whose magnitude may be as much as - 50 microamperes (at an applied indicator potential

of 150 millivolts). After thirty seconds, however, the current reverses and increases to a constant value, that is to the limiting diffusion current for the particular initial hydrogen ion concentration. This behavior can be explained as follows: Initially oxygen is adsorbed on the indicator anode and hydrogen is adsorbed on the indicator cathode. The combined effects change the potentials of the individual electrodes until they approach the applied potential and very little current flows between the electrodes. However, when hydrogen gas is bubbled through the stirred solution, more hydrogen is adsorbed on the cathode causing a larger back e.m.f. which produces the observed current reversal. The adsorbed oxygen on the indicator anode will be reduced to water during the reversal and the quantity of oxygen adsorbed limits the time of the current reversal.

When the adsorbed oxygen is removed from the electrode surface, the diffusion-controlled electrode processes occur. At the indicator cathode,

$$2H^+ \rightarrow 2H - 2e^- \qquad 2H \rightarrow H_2$$

and at the indicator anode,

$$H_2 \rightarrow 2H^+ + 2e^-$$

By diminishing the indicator cathode size relative to that of the anode, the indicator current is limited by the diffusion and discharge of the hydrogen ions and the current is observed to be proportional to the hydrogen ion concentration.

At pH values between 5 and 8, depending upon the applied indicator potential, a minimum followed by a steep linear portion is observed in the plot of indicator current vs. time of hydroxide generation. It is assumed that near pH 7, the hydrogen ion concentration becomes so small that another diffusion-controlled electrode process is the process limiting the indicator current.

In Figure 2, the indicator current rise following the minimum shows a slope greater than the decreasing slope. When the polarity of the indicator electrodes were reversed or a small platinized-platinum wire was used as the indicator anode, the current rose with a very much smaller slope. Since the diffusion current depends upon the size of the limiting indicator electrode, it was concluded that diffusion to the anode exercised control over the indicator current.

An explanation of this indicator current rise may be made by the following electrode reactions:

At the indicator anode,

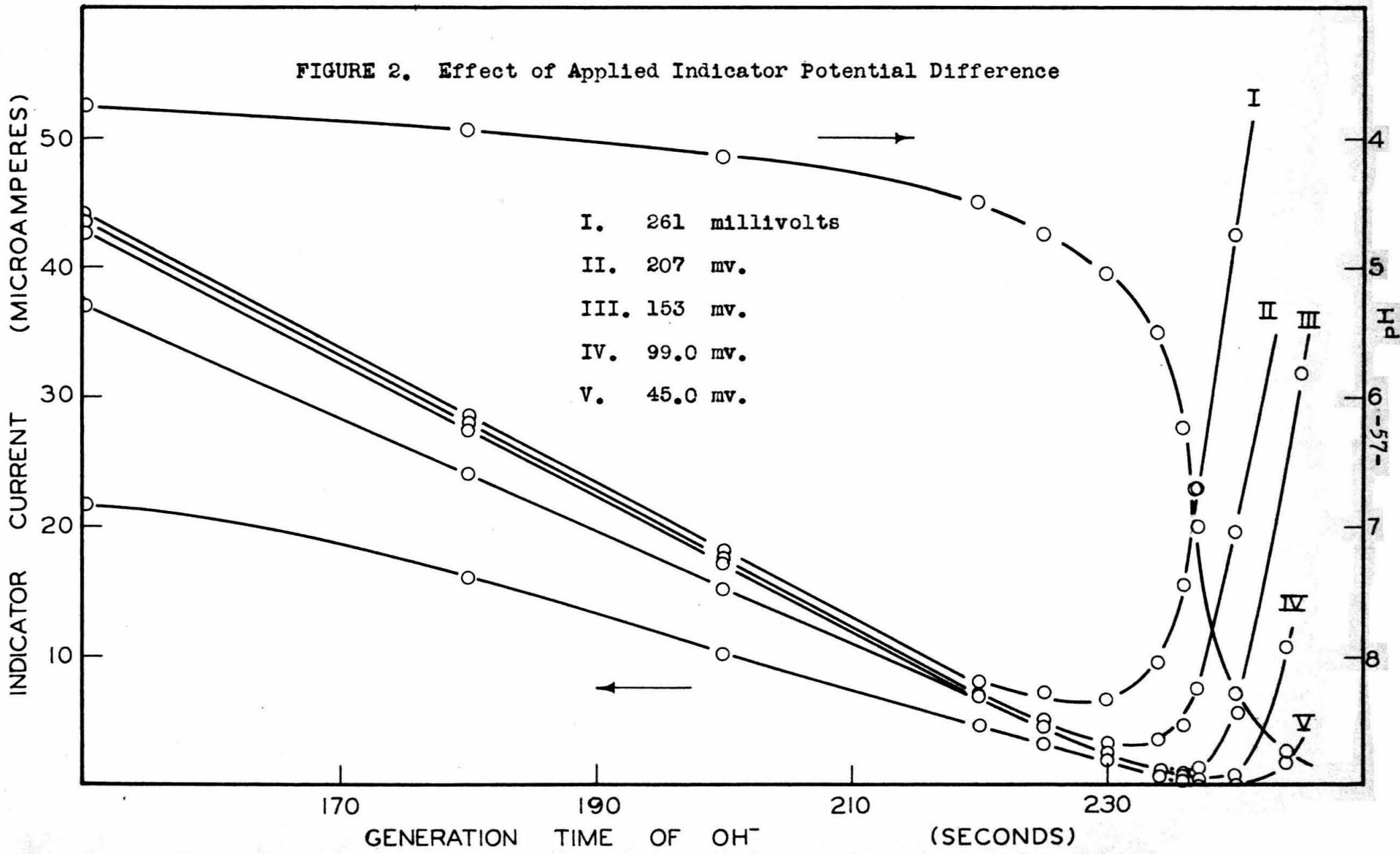
$$H_2 + 2OH^- - 2e^- \rightarrow 2H_2O$$

At the indicator cathode,

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

As the hydrogen ion concentration decreases, the indicator current is controlled first by diffusion of the hydrogen ions to the indicator cathode and the current decreases linearly with the hydrogen ion concentration. At a pH near seven, depending upon the applied potential and the indicator

FIGURE 2. Effect of Applied Indicator Potential Difference



electrode sizes, the half-cell reactions given above occur. Water rather than hydrogen ions is reduced at the indicator cathode with the reverse half-cell reaction taking place at the indicator anode. Since the water concentration remains constant, the diffusion of hydroxide ions to the anode determines the indicator current.

As a test of the proposed mechanism, the effect of the removal of hydrogen gas was studied. When nitrogen was bubbled through the solution, sweeping out the hydrogen as rapidly as it was formed at the generator cathode, erratic indicator currents resulted throughout the titration. The currents were below ten microamperes and did not show the uniform slopes observed when hydrogen was present.

Effect of Applied Indicator Potential

The indicator electrode processes postulated for the observed indicator currents in this study of hydrogen ions and hydrogen gas, and those suggested in similar studies of solutions containing a halogen and the corresponding halide or cuprous and cupric copper have involved the same half-cell reaction proceeding in opposite directions at the two indicator electrodes. Thus, the only energy expended by the applied potential was that required to overcome overvoltages and the ohmic resistance of the solution.

Experiments have shown that a definite potential difference is necessary to establish the reversible half-cell reactions at the indicator electrodes. Since one of the components of the half-cell reaction is in smaller concentration,

(hydrogen ion in this study, the hydrogen gas being kept constant), there is a potential at which current will be limited by the rate at which hydrogen ions can diffuse to the indicator cathode. Essentially no increase in the current with increase in the applied potential will be observed until a potential is reached at which another process can occur. In the presence of excess hydrogen gas, there will be no effect on the indicator current produced by slight variations of applied potential difference until a value is reached when the solution is electrolyzed at the indicator electrodes.

To determine the hydrogen ion concentration corresponding to the minimum indicator current, the pH and the indicator current were measured simultaneously during a titration by means of a small Beckmann # 290-11X glass electrode and a Beckmann # 270-6 calomel electrode, which were fixed in the titration cell and attached to a Beckmann Model H pH Meter. A solution 0.001 VF in hydrochloric acid containing potassium chloride 0.1 VF was placed in a titration cell and saturated with hydrogen gas. Hydroxyl ions were generated at a constant rate to definite hydrogen ion concentrations indicated by the pH meter. At each stop, the indicator potential was varied from zero to 261 millivolts and the indicator currents were observed. Figures 3. and 4. show the indicator current vs. applied potential at fixed hydrogen ion concentrations. Figure 2. is the same data plotted as indicator current vs. generation time of hydroxyl ion (which is proportional to the hydrogen ion concentration).

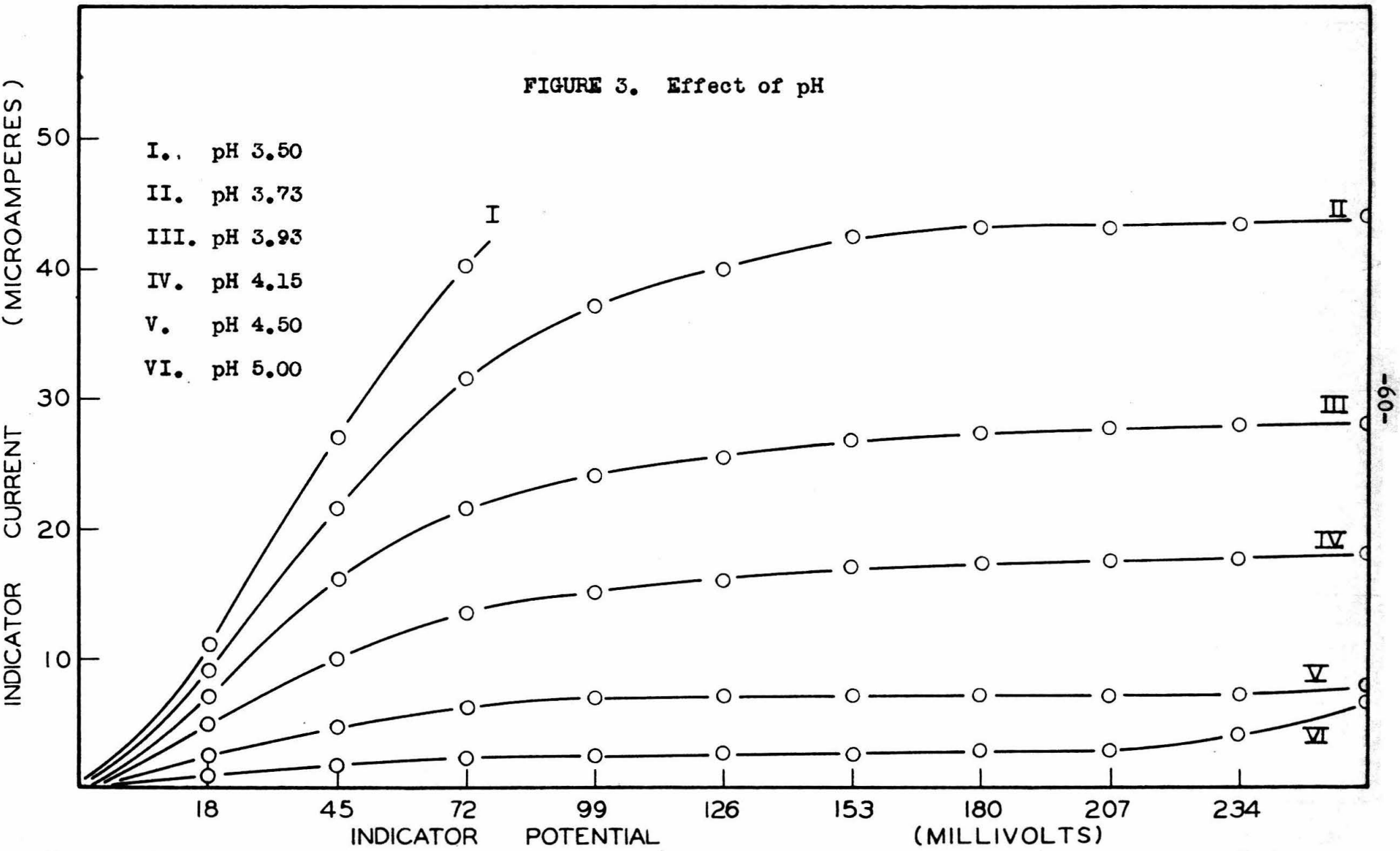
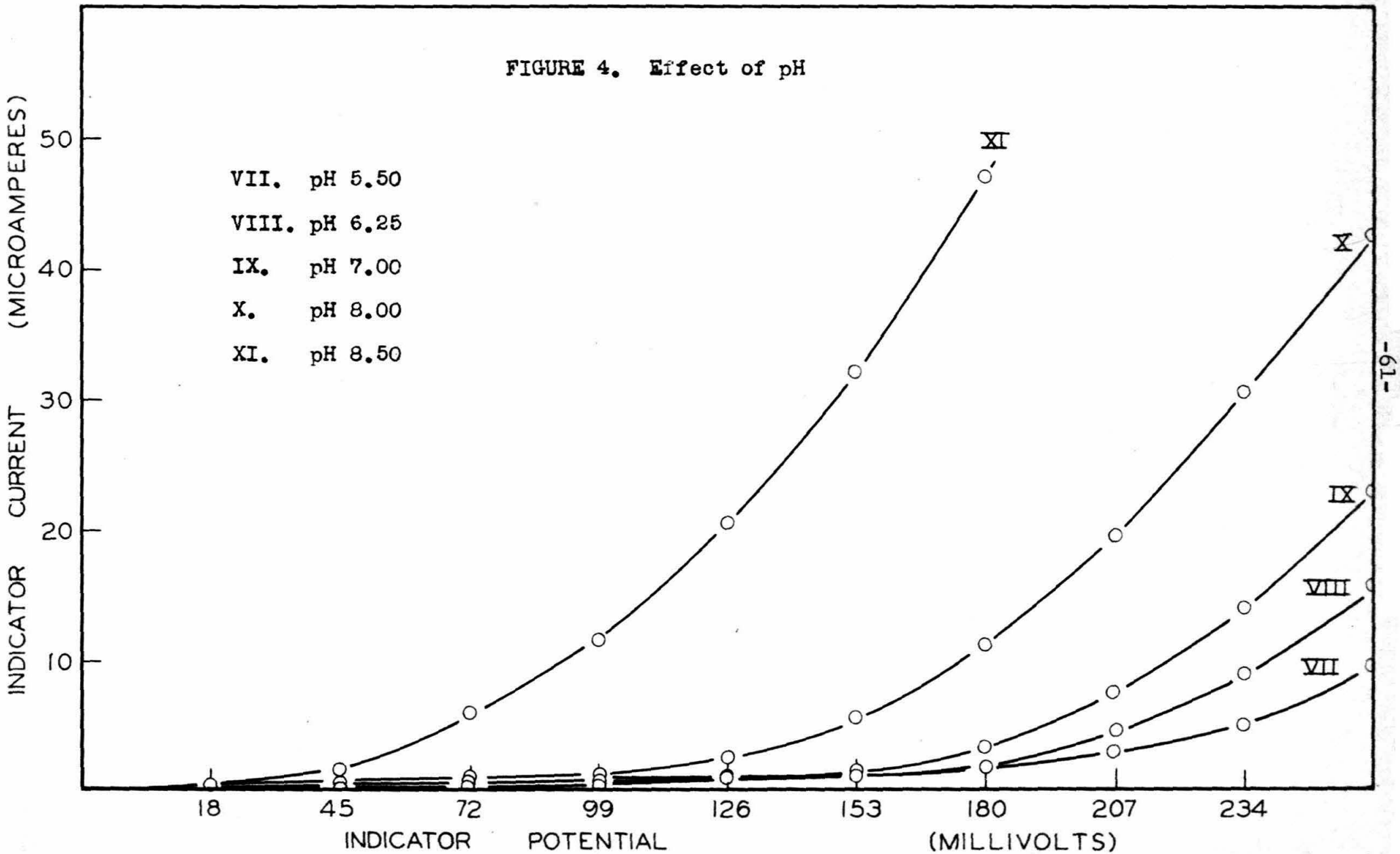


FIGURE 3. Effect of pH
I. pH 3.50
II. pH 3.73
III. pH 3.93
IV. pH 4.15
V. pH 4.50
VI. pH 5.00
INDICATOR CURRENT (MICROAMPERES)
50
40
30
20
10
I
II
III
IV
V
VI
18
45
72
99
126
153
180
207
234
INDICATOR POTENTIAL (MILLIVOLTS)

FIGURE 4. Effect of pH



The magnitudes of the indicator current at fixed hydrogen ion concentrations depend upon the size of the electrode at which the limiting process is occurring, upon the diffusion coefficient of the controlling substance and upon the concentration of the diffusing substance. For this reason, the transition between electrode processes would not be expected to occur at a time corresponding to equal concentrations of hydrogen and hydroxyl ions. The minima in the curves show a marked dependence upon the indicator potential. At higher potentials, the minima are shifted markedly toward higher hydrogen ion concentrations while at small potentials (less than 125 millivolts) the minima are broad and a precise determination of the minimum point is difficult, but the minimum lies near to pH 7.

Effect of Oxygen

In a titration of hydrochloric acid, the hydrogen gas tube was removed from the titration cell and oxygen gas was bubbled through the solution. A rapid increase in the indicator current to values greater than fifty microamperes was observed. Within twenty seconds, however, the current decreased to two microamperes. Further addition of oxygen gas produced no effect. If the polarity of the indicator electrodes were reversed, one observed a greater value for the indicator current when the oxygen was added.

These facts suggest an electrode process in which the indicator cathode controls the current flow. The facts are explained by the following reactions:

At the indicator cathode,

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

At the indicator anode,

$$2H_2O - 4e^- \rightarrow O_2 + 4H^+$$

The increase in oxygen gas concentration upon passing the gas into the solution would account for the observed current increase. However, the current would continue to flow until the concentration of hydrogen ions in the diffusion layer was depleted. The current no longer would be controlled by diffusion of oxygen to the indicator cathode but by the diffusion of hydrogen ions. Since there is no hydrogen gas diffusing to the anode the current decreases to a small value. When the oxygen gas delivery tube was removed and hydrogen gas was again bubbled into the solution, a current reversal occurred. The same mechanism described above for the initial reversal is appropriate in this case. By shorting the electrodes momentarily, the current reversal was rapidly overcome and the limiting diffusion current was obtained again.

These phenomena are observed at all of the hydrogen ion concentrations studied during a titration.

Effect of Bright Platinum Electrodes

When bright platinum indicator electrodes were used an initial surge of current was observed as the indicator potential difference was applied, which diminishes to about ten microamperes and remained near to this value throughout the titration. In general, currents obtained with smooth electrodes

did not show the great sensitivity toward small changes in the hydrogen ion concentration that was obtained with platinized-platinum electrodes.

Indicator current phenomena obtained when a small platinized-platinum cathode was used with a large smooth platinum anode were similar to those observed with platinized-platinum electrodes. However, at hydrogen ion concentrations near neutral, depending upon the applied potential, serious current reversals occurred which could not be rapidly overcome. It was difficult to observe diffusion currents in that case.

Titration Procedure

As an application of the hydrogen ion-controlled diffusion current phenomena, a coulometric titration procedure for strong acids has been studied which is based upon the electro-generation of hydroxyl ion at a constant current using the diffusion current for the determination of the end-point.

Solutions for titration were prepared by pipetting twenty-five milliliters of the standard dilute acid into a titration cell containing five milliliters of 1 VF potassium chloride and ten milliliters of water. The cell was attached to the apparatus, the stirring begun and hydrogen gas bubbled through the solution for thirty seconds. The indicator potential difference was applied and about thirty seconds were allowed for the current reversal and the establishment of the limiting diffusion current. A reading was taken and the indicator circuit was opened. The indicator potential difference was not

applied during the generation since extraneous currents were induced in the indicator circuit. The generator current passing through the dummy resistance was adjusted to the desired value and hydroxyl ions were generated. At each pause in generation, the indicator circuit was closed and readings were taken. Near to the minimum in the indicator current vs. time plot, the generation was done in five second intervals.

It was found the continuous bubbling of hydrogen gas through the solution during the generation of hydroxyl ions was not necessary after the initial saturation. However, as a precaution against absorption of carbon dioxide by the solution, hydrogen gas was maintained over the solution and the gas was bubbled through the solution occasionally during the titration.

A plot of the indicator current vs. time of generation was made and the initial linear portion of the plot (from 5 to 40 microamperes) was extrapolated forward to zero indicator current giving the titration time.

Blank solutions containing five milliliters 1 VF potassium chloride and thirty-five milliliter of water were similarly titrated. In the preparation of the potassium chloride solution sufficient 0.1 VF hydrochloric acid had been added to produce a pH of about four so that at least two points on the linear portion of the curve could be obtained for extrapolation to zero current. This correction time was subtracted from the sample titration time giving the corrected titration time.

It was found that washing the electrodes with water following each titration of a sample or blank was not sufficient to remove hydroxyl ions adsorbed on the electrode assembly and low results were obtained in successive determinations. Consequently, the electrodes were rinsed with 0.01 VF sulfuric acid and washed carefully with distilled water. After several titrations the indicator electrodes were shorted to the generator cathode and hydrogen was generated over the surfaces. This procedure could be conveniently accomplished in conjunction with the removal of the silver chloride from the surface of the silver wire anode by reversing the polarity of the generator electrodes and electrolyzing the dilute sulfuric acid solution.

Coulometric Titration of Hydrochloric Acid

In Table I.are shown the data from a series of titrations of dilute hydrochloric acid solutions.

Disagreement of several percent with the theoretical titration times were observed in the titration time of these solutions. Experiments indicated that the observed times agreed well with the generation times determined by a potentiometric end-point. It was concluded that these errors were not to be attributed to the end-point method but to changes in the hydrogen ion concentration occurring between the preparation of the solution and the titration.

When the samples were titrated to a pH of about nine and the electrodes were washed with water between titrations, consistently low results were obtained. This fact has been interpreted as the result of adsorption of hydroxyl ions on the electrodes from a previous sample.

Washing the electrodes with 0.01 VF sulfuric acid between titrations eliminated this source of error, although the results were critically dependent upon thorough rinsing of the electrodes with water.

The data indicate the profitable use of the hydrogen ion-controlled diffusion current for the determination of end-points of coulometric titrations of strong acids. The generation rate of the apparatus was so small that only extremely dilute solutions of acid could be conveniently titrated coulometrically, and in these cases errors resulting from absorption of carbon dioxide and from incomplete washing were significant. However, it was thought that this end-point technique was more sensitive and precise than the confirmatory titrations implied and could be successfully used with titrations of more concentrated acids and bases. In Table II. are shown the results of comparison titrations of twenty-five milliliters of 0.2 VF hydrochloric acid with 0.2 VF sodium hydroxide using the amperometric end-point and the methyl orange end-point.

TABLE I

Coulometric Titrations of Hydrochloric Acid

Sample: Hydrochloric Acid

Potassium Chloride 0.1 VF

Solution Volume: 40 milliliters

Generation Rate: 1.0385×10^{-7} equivalents per second

Current Density: 40.0 milliamper/square centimeter

Theoretical Time	Average Blank Time	Corrected Titration Time
237.7 second	17.5 seconds	240 seconds 237 238
237.7	22.0	242 241 233 234
237.7	23.0	239 237 235
119.0	28.0	117 120 119 118 119 123

TABLE II

Titration of 0.2 VF Hydrochloric Acid with 0.2 VF Sodium Hydroxide

Volume of HCl	Volume of NaOH	End-Point
24.98 ml.	25.46 ml.	Methyl Orange
	25.46	" "
	25.45	" "
	25.47	" "
24.98 ml	25.46 ml.	Diffusion Current
	25.47	" "
	25.45	" "
	25.46	" "

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